

TITLE OF INVENTION

FLAME RETARDANT FIBER BLENDS COMPRISING MODACRYLIC
FIBERS AND FABRICS AND GARMENTS MADE THEREFROM

BACKGROUND OF THE INVENTION

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There is an ongoing need for flame retardant, also referred to as fire resistant, fabrics that can be used to make clothing suitable for people who work near flames, high temperatures, or electric arc flashes. In addition to showing excellent thermal performance, an effective flame

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retardant fabric should be durable, comfortable, and produced at low cost.

Although fabrics made of inherently flame retardant fibers have been very useful in protective garments, certain characteristics of these fibers

present problems. For instance, these fibers can be difficult to dye,

provide uncomfortable fabric textures, and are expensive. To address

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these problems, inherently flame retardant fibers have been blended with

fibers made of other materials. Fiber blending can be used to obtain an

end fabric that combines the beneficial characteristics of each of the

constituent fibers. However, such blending often comes at the expense of durability and thermal performance.

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Certain fiber blends and fabrics made from those blends are known

in the art. For instance, U.S. Patent No. 4,920,000 (Green) issued on April

24, 1990 discloses a durable heat resistant fabric comprising certain

blends of cotton, nylon, and heat resistant fibers. U.S. Patent No.

4,970,111 (Smith, Jr.) issued November 13, 1990 discloses a fire resistant

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fabric comprising a blend of chlorine-containing polymeric fibers,

polyacrylonitrile fibers, and a fire retarding polyester binder. U.S. Patent

- No. 5,503,916 (Ichibori et al.) issued April 2, 1996 discloses flame retardant clothing comprising natural or chemical fibers and a polymer fiber containing antimony and halogen compounds. U.S. Patent No. 6,132,476 (Lunsford et al.) issued October 17, 2000 discloses dyed fabric blends containing inherently flame retardant fibers and flame retardant cellulosic fibers containing a flame retardant compound. U.S. Patent No. 6,254,988 B1 (Zhu et al.) issued on July 3, 2001 discloses a fabric composed of particular blends of cotton, nylon, and para-aramid fibers that is comfortable, cut resistant, and abrasion resistant. U.S. Patent Application Publication No. 2001/0009832 A1 (Shaffer et al.) published on July 26, 2001 discloses a flame retardant fabric comprising dissimilar warp and fill yarns wherein the warp yarns comprise staple or filament fibers and have a Limiting Oxygen Index of at least 27, the fill yarns comprise natural fibers, and the ratio of warp to fill yarn ends in the fabric is at least 1.0. U.S. Patent No. 6,547,835 B1 (Lunsford et al.) issued on April 15, 2003 discloses a method for dyeing flame retardant fabrics.

Fabrics made from the fiber blends and yarns discussed above either naturally suffer from poor resistance to abrasion or, as disclosed in U.S. Patent No. 4,920,000 (Green) issued on April 24, 1990, utilize a large percentage of cotton fiber, which has very low abrasion resistance. Fire protective clothing and garments are normally used in harsh environments so any improvement in abrasion resistance of the fabrics used in those garments is important and desired. There is therefore, a need for flame retardant fiber blends, yarns, and fabrics that have improved abrasion resistance.

SUMMARY OF THE INVENTION

In accordance with the purpose of the invention, as embodied and broadly described herein, the invention is an intimate blend of staple fibers comprising 10 to 75 parts by weight of at least one aramid staple fiber, 15
5 to 80 parts by weight of at least one modacrylic staple fiber, and 5 to 30 parts by weight of at least one polyamide staple fiber.

In another embodiment, the invention is an intimate blend of staple fibers comprising 20 to 40 parts by weight of at least one aramid staple fiber, 50 to 80 parts by weight of at least one modacrylic staple fiber, and
10 15 to 20 parts by weight of at least one polyamide staple fiber.

In another embodiment, the invention is one of the intimate blends described above, wherein the at least one aramid staple fiber is poly(metaphenylene isophthalamide) and the at least one modacrylic staple fiber is a copolymer of acrylonitrile and vinylidene chloride.

15 The modacrylic staple fiber of this invention preferably contains an antimony additive. The preferred antimony additive is an antimony oxide.

The intimate blends of this invention may be used to make a yarn, which in turn may be used to make a flame retardant fabric for use in flame retardant articles such as clothing.

20 Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating embodiments of the invention, are given by way of illustration only, because various changes and modifications within the
25 spirit and scope of the invention will become apparent to those skilled in

the art from this detailed description. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

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DETAILED DESCRIPTION

There is an ongoing need for fiber blends from which flame retardant, also referred to as fire resistant, fabrics can be made that can be used to make clothing and other articles suitable for people who work near flames, high temperatures, or electric arc flashes, and the like.

10 Considerable effort has been made to increase the effectiveness of such fiber blends and the resulting fabrics, while maintaining or improving their comfort and durability and reducing their overall cost. The present invention represents just such an advance in the field of flame retardant garments.

15 An intimate blend of staple fibers of this invention comprises aramid fibers, modacrylic fibers, and polyamide fibers. The proportions of each component are important to achieve the necessary combination of physical qualities. By "intimate blend" is meant that two or more fiber classes are blended prior to spinning a yarn. In the present invention, the
20 intimate blend is formed by combining aramid fibers, modacrylic fibers, and polyamide fibers in the fiber form, and then spinning into a single strand of yarn. By "yarn" is meant an assemblage of fibers spun or twisted together to form a continuous strand, which can be used in weaving, knitting, braiding, or plaiting, or otherwise made into a textile material or
25 fabric. Such yarns can be made by conventional methods for spinning

staple fibers into yarns, such as, for example, ring-spinning, or higher speed air spinning techniques such as Murata air-jet spinning where air is used to twist the staple into a yarn.

The intimate blend of staple fibers of this invention includes aramid
5 fibers, which are inherently flame retardant. By "aramid fiber" is meant one or more fibers made from one or more aromatic polyamides, wherein at least 85% of the amide (-CONH-) linkages are attached directly to two aromatic rings. Aromatic polyamides are formed by reactions of aromatic diacid chlorides with aromatic diamines to produce amide linkages in an
10 amide solvent. Aramid fibers may be spun by dry or wet spinning using any number of processes, however, U.S. Patent Nos. 3,063,966; 3,227,793; 3,287,324; 3,414,645; 3,869,430; 3,869,429; 3,767,756; and 5,667,743 are illustrative of useful spinning processes for making fibers that could be used in this invention.

15 Aramid fibers are typically available in two distinct classes, namely meta-aramid fibers, or m-aramid fibers, one of which is composed of poly(metaphenylene isophthalamide), which is also referred to as MPD-I, and para-aramid fibers, or p-aramid fibers, one of which is composed of poly(paraphenylene terephthalamide), also referred to as PPD-T. Meta-
20 aramid fibers are currently available from E. I. du Pont de Nemours of Wilmington, Delaware in several forms under the trademark NOMEX®: NOMEX T-450® is 100% meta-aramid; NOMEX T-455® is a blend of 95% NOMEX® and 5% KEVLAR® (para-aramid); and NOMEX IIIA® (also known as NOMEX T-462®) is 93% NOMEX®, 5% KEVLAR®, and 2%
25 carbon core nylon. In addition, meta-aramid fibers are available under the

trademarks CONEX® and APYEIL® which are produced by Teijin, Ltd. of Tokyo, Japan and Unitika, Ltd. of Osaka, Japan, respectively. Para-aramid fibers are currently available under the trademarks KEVLAR® from E.I. du Pont de Nemours of Wilmington, Delaware and TWARON® from Teijin Ltd. of Tokyo, Japan. For the purposes herein, TECHNORA® fiber, which is available from Teijin Ltd. of Tokyo, Japan, and is made from copoly(p-phenylene/3,4'diphenyl ester terephthalamide), is considered a para-aramid fiber.

In one embodiment of this invention, the at least one aramid staple fiber is poly(metaphenylene isophthalamide).

The intimate blend of staple fibers of this invention also includes modacrylic fibers. Modacrylic fibers are manufactured fibers in which the fiberforming substance is any long chain synthetic polymer composed of less than 85%, but at least 35%, by weight of acrylonitrile ($-\text{CH}_2\text{CH}[\text{CN}]-$)_x units. Modacrylic fibers are made from resins that are copolymers (combinations) of acrylonitrile and halogen-containing compounds, such as vinyl chloride, vinylidene chloride or vinyl bromide. Modacrylic fibers are inherently flame retardant because they are copolymerized with these other compounds such as vinyl chloride, vinylidene chloride, or vinyl bromide. Modacrylic fibers are commercially available under various trademarks, such as Protex® (ACN/polyvinylidene chloride co-polymer), which is available from Kaneka Corporation of Osaka, Japan.

In one embodiment of this invention, the at least one modacrylic fiber is a copolymer of acrylonitrile and vinylidene chloride.

The modacrylic staple fibers of this invention preferably contain an antimony additive. The preferred antimony additive is an antimony oxide, preferably added in an amount greater than two percent by weight.

The intimate blend of staple fibers of this invention also includes
5 polyamide fibers. By "polyamide fibers" is meant one or more fibers made from one or more aliphatic polyamide polymers, generically referred to as nylon. Examples include polyhexamethylene adipamide (nylon 66), polycaprolactam (nylon 6), polybutyrolactam (nylon 4), poly(9-aminononanoic acid) (nylon 9), polyenantholactam (nylon 7),
10 polycapryllactam (nylon 8), and polyhexamethylene sebacamide (nylon 6, 10). Nylon fibers are generally spun by extrusion of a melt of the polymer through a capillary into a gaseous congealing medium. When nylon is the polyamide fiber in the intimate blend of staple fibers forming a yarn, such yarn preferably is used as the warp yarn when forming a fabric to enhance
15 protection against soft surface abrasion in the finished fabric or garment made from such fabric. In one embodiment of this invention, when nylon is used in this manner to make the fabrics or garments of this invention, the fabrics or garments of this invention are expected to have more than ten percent higher resistance to abrasion compared to similar fabrics
20 without nylon, as measured in cycles to failure according to the Abrasion Resistance Test described below. However, too much nylon in a fabric will cause the fabric to become stiff and lose drape when the fabric is exposed briefly to high temperatures.

In one embodiment of this invention, nylon fiber has a linear density
25 from 1 to 3 dtex. In another embodiment the nylon fiber has a linear

density from 1 to 1.5 dtex. In yet another embodiment the nylon fiber has a linear density of about 1.1 dtex.

The intimate blend of staple fibers of this invention can be used to make yarns and fabrics that are flame retardant. These yarns and fabrics
5 can be used to make flame retardant articles, such as flame retardant garments and clothing, which are particularly useful for firefighters and other workers who are put in close proximity to flames, high temperatures, or electric arc flashes. Generally, by "flame retardant" is meant that the fabric does not support flame in air after coming in contact with a flame for
10 a short period of time. More precisely, "flame retardant" can be defined in terms of the Vertical Flame Test, described below. Flame retardant fabrics preferably have a char length of less than six inches after a twelve second exposure to a flame. The terms "flame retardant," "flame resistant," "fire retardant," and "fire resistant" are used interchangeably in
15 the industry, and references to "flame retardant" compounds, fibers, yarns, fabric, and garments in the present invention could be described identically as "flame resistant," "fire retardant," or "fire resistant."

Staple fibers for use in spinning yarns are generally of a particular length and of a particular linear density. For use in this invention,
20 synthetic fiber staple lengths of 2.5 to 15 centimeters (1 to 6 inches) and as long as 25 centimeters (10 inches) can be used, and lengths of 3.8 to 11.4 centimeters (1.5 to 4.5 inches) are preferred. Yarns made from such fibers having staple lengths of less than 2.5 centimeters have been found to require excessively high levels of twist to maintain strength for
25 processing. Yarns made from such fibers having staple lengths of more

than 15 centimeters are more difficult to make due to the tendency for long staple fibers to become entangled and broken, resulting in short fibers.

The synthetic staple fibers can be crimped or not, as desired for any particular purpose. The staple fibers of this invention are generally made

5 by cutting continuous filaments to certain predetermined lengths.

However, staple fibers can be made by other means, such as by stretch-breaking, and yarns can be made from such fibers as well as from a variety or distribution of different staple fiber lengths.

In one embodiment of this invention, the yarn of this invention can
10 be used to make a flame retardant fabric, which is a cloth produced by weaving, knitting, or otherwise combining the yarn of this invention. Flame retardant fabrics can be constructed having warp yarn comprising the yarns of this invention, fill yarn comprising the yarns of this invention, or both warp and fill yarns comprising the yarns of this invention. When
15 fabrics use the yarn of this invention in only one direction (i.e., as only fill or only warp), other suitable yarns may be used in the other direction according to the desired fabric characteristics. For best abrasion resistance, the yarn of this invention is used in the warp direction since warp yarn typically forms most of the direct contact surface of a fabric.
20 This translates into better abrasion performance of the outer surface of the fabric in garment form.

In one embodiment of this invention, the flame retardant fabric has a basis weight of from 4 and 15 ounces per square yard. In another embodiment of this invention the flame retardant fabric has a basis weight
25 of from 5.5 to 11 ounces per square yard. Such fabrics can be made into

articles of clothing, such as shirts, pants, coveralls, aprons, jacket, or any other single or multi-layer form for flash fire or electric arc protection.

The articles of the invention will be further described below with reference to the working examples. It should be noted however that the
5 concept of the invention will not be limited at all by these examples.

TEST METHODS

The following test methods were used in the following Examples.

Thermal Protective Performance Test (TPP). The predicted protective performance of a fabric in heat and flame was measured using
10 the "Thermal Protective Performance Test" (NFPA 2112). A flame was directed at a section of fabric mounted in a horizontal position at a specified heat flux (typically 84 kW/m^2). The test measures the transmitted heat energy from the source through the specimen using a copper slug calorimeter with no space between the fabric and heat source.
15 The test endpoint was characterized by the time required to attain a predicted second-degree skin burn injury using a simplified model developed by Stoll & Chianta, "Transactions New York Academy Science", 1971, 33 p 649. The value assigned to a specimen in this test, denoted as the "TPP value," is the total heat energy required to attain the endpoint, or
20 the direct heat source exposure time to the predicted burn injury multiplied by the incident heat flux. Higher TPP values denote better insulation performance.

Vertical Flame Test. The "Vertical Flame Test" (ASTM D6413) is generally used as a screening test to determine whether a fabric burns, as
25 a predictor for whether an article of clothing has any flame retarding

properties. According to the test, a 3 x 12 inch section of fabric was mounted vertically and a specified flame was applied to its lower edge for twelve seconds. The response of the fabric to the flame exposure was recorded. The length of the fabric that was burned or charred was

5 measured. Times for afterflame (i.e., the continued burning of the fabric section after removing the test flame) and afterglow (characterized by smoldering of the fabric section after removing the test flame) were also measured. Additionally, observations regarding melting and dripping from the fabric section were recorded. Pass/fail specifications based on this

10 method are known for industrial worker clothing, firefighter turnout gear and flame retardant station wear, and military clothing. According to industry standards, a fabric can be considered flame retardant, or fire resistant, if it has a char length of less than six inches after a twelve second exposure to a flame.

15 Abrasion Resistance Test. Abrasion resistance was determined using ASTM method D3884, with a H-18 wheel, 500 gms load on a Taber abrasion resistance meter available from Teledyne Taber, 455 Bryant St., North Tonawanda, N.Y. 14120. Taber abrasion resistance was reported as cycles to failure.

20 Tear Strength Test. The tear strength measurement is based on ASTM D 5587. The tear strength of textile fabrics was measured by the trapezoid procedure using a recording constant-rate-of-extension-type (CRE) tensile testing machine. Tear strength, as measured in this test method, requires that the tear be initiated before testing. The specimen

25 was slit at the center of the smallest base of the trapezoid to start the tear.

The nonparallel sides of the marked trapezoid were clamped in parallel jaws of a tensile testing machine. The separation of the jaws was increased continuously to apply a force to propagate the tear across the specimen. At the same time, the force developed was recorded. The
5 force to continue the tear was calculated from autographic chart recorders or microprocessor data collection systems. Two calculations for trapezoid tearing strength were provided: the single-peak force and the average of five highest peak forces. For the examples here, the single-peak force was used.

10 Grab Strength Test. The grab strength measurement, which is a determination of breaking strength and elongation of fabric or other sheet materials, is based on ASTM D5034. A 100 mm (4.0 in.) wide specimen was mounted centrally in clamps of a tensile testing machine and a force applied until the specimen broke. Values for the breaking force and the
15 elongation of the test specimen were obtained from machine scales or a computer interfaced with testing machine.

EXAMPLES

Example 1 is a fabric of this invention comprising an intimate blend of this invention for both the warp and fill yarns. Example 2 is a fabric of
20 this invention comprising an intimate blend of this invention for the warp yarn and an intimate blend of aramid and modacrylic, for the fill yarn. Comparative Example A is not a fabric of this invention, but instead comprises an intimate blend of aramid and modacrylic, with no nylon, for both the warp and fill yarns. Following are more detailed descriptions of
25 these examples, followed by test results for each example.

Example 1. A comfortable and durable fabric was prepared with warp and fill ring spun yarns comprising an intimate blend of Nomex® type 462, modacrylic, and nylon. Nomex® type 462 is 93% poly(m-phenylene isophthalamide)(MPD-I), 5% poly(p-phenylene terephthalamide)(PPD-T) and 2% static dissipative fibers (Type P-140, available from E. I. du Pont de Nemours of Wilmington, Delaware). The modacrylic fibers in this example were ACN/polyvinylidene chloride co-polymer (available under the trademark Protex®, from Kaneka Corporation of Osaka, Japan), and the nylon used was polyhexamethylene adipamide.

A picker blend sliver of 35 weight percent of Nomex® type 462, 50 weight percent of the modacrylic and 15 weight percent of the nylon was prepared and processed by the conventional cotton system into a spun yarn having twist multiplier of 3.7 using a ring spinning frame. The yarn so made was a 24.6 tex (24 cotton count) single yarn. Two single yarns were then plied on a plying machine to make a two-ply yarn for use as a warp yarn. Using a similar process and the same twist and blend ratio, a 32.8 tex (18 cotton count) single yarn was made and then two of these yarns were plied for use as a fill yarn.

The Nomex®/modacrylic/nylon yarns were used as the warp and fill in a shuttle loom in a 3x1 twill construction. The greige twill fabric had a construction of 24 ends x 15 picks per cm (60 ends x 39 picks per inch), and basis weight of 271.3 g/m² (8 oz/yd²). The greige twill fabric prepared as described above was scoured in hot water and dried under low tension. The scoured fabric was then dyed using acid dye. The finished fabric was

then tested for its thermal and mechanical properties. The results of these tests are shown in Table 1.

Example 2

A comfortable and durable fabric was prepared comprising ring spun warp yarns made from an intimate blend of Nomex® type 462, modacrylic, and nylon, and ring spun fill yarns made from intimate blends of Nomex® type 462 and modacrylic.

Nomex® type 462 is 93% poly(m-phenylene isophthalamide)(MPD-I), 5% poly(p-phenylene terephthalamide)(PPD-T) and 2% static dissipative fibers (Type P-140, available from E. I. du Pont de Nemours of Wilmington, Delaware). The modacrylic in this example was ACN/polyvinylidene chloride co-polymer (available under the trademark Protex®, from Kaneka Corporation of Osaka, Japan), and the nylon used was polyhexamethylene adipamide.

A picker blend sliver of 35 weight percent of Nomex® type 462, 50 weight percent of the modacrylic and 15 weight percent of the nylon was prepared and processed by the conventional cotton system into a spun yarn having twist multiplier of 3.7 using a ring spinning frame. The yarn so made was a 24.6 tex (24 cotton count) single yarn. Two single yarns were then plied on a plying machine to make a two-ply yarn for use as a warp yarn. Using a similar process and the same twist, a 32.8 tex (18 cotton count) single yarn with a blend of 50 weight percent Nomex® type 462 and 50 weight percent of the modacrylic was made and then two of these single yarns were plied for use as a fill yarn.

The Nomex®/modacrylic/nylon yarn was used as the warp and the Nomex®/modacrylic yarn was used as the fill in a shuttle loom in a 3x1 twill construction. The greige twill fabric had a construction of 23 ends x 16 picks per cm (58 ends x 40 picks per inch), and basis weight of 264.5 g/m² (7.8 oz/yd²). The greige twill fabric prepared as described above was scoured in hot water and dried under low tension. The scoured fabric was then dyed using acid dye. The finished fabric was then tested for its thermal and mechanical properties. The results of these tests are shown in Table 1.

10 **Comparative Example A**

A comfortable and durable fabric was prepared comprising ring spun warp yarns made from an intimate blend of Nomex® type 462 and modacrylic and ring spun fill yarns made from an intimate blend of Nomex® type 462 and modacrylic.

15 Nomex® type 462 is 93% poly(m-phenylene isophthalamide)(MPD-I), 5% poly(p-phenylene terephthalamide)(PPD-T) and 2% static dissipative fibers (Type P-140, available from E .I. du Pont de Nemours of Wilmington, Delaware). The modacrylic in this example was ACN/polyvinylidene chloride co-polymer (available under the trademark
20 Protex® from Kaneka Corporation of Osaka, Japan).

A picker blend sliver of 50 weight percent of Nomex® type 462 and 50 weight percent of the modacrylic was prepared and processed by the conventional cotton system into a spun yarn having twist multiplier of 3.7 using a ring spinning frame. The yarn so made was a 24.6 tex (24 cotton
25 count) single yarn. Two of these single yarns were then plied on a plying

machine to make a two-ply yarn for use as a warp yarn. Using a similar process and the same twist, a 32.8 tex (18 cotton count) single yarn with a blend of 50 weight percent Nomex® type 462 and 50 weight percent of the modacrylic was made and then two of these single yarns were plied for

5 use as a fill yarn.

The Nomex®/modacrylic yarn was used as the warp and the fill in a shuttle loom in a 3x1 twill construction. The greige twill fabric had a construction of 23 ends x 15 picks per cm (58 ends x 38 picks per inch), and basis weight of 254 g/m² (7.5 oz/yd²). The greige twill fabric prepared

10 as described above was scoured in hot water and dried under low tension. The scoured fabric was then dyed using acid dye. The finished fabric was then tested by its thermal and mechanical properties. The results of these tests are shown in Table 1.

Table 1. Example Test Results

Example No.		Example 1	Example 2	Comparative Example A
Fabric Design	Warp Yarn	NOMEX®/Protex®/Nylon 35/50/15% by Weight	NOMEX®/Protex®/Nylon 35/50/15% by Weight	NOMEX®/Protex® 50/50% by Weight
	Fill Yarn	NOMEX®/Protex®/Nylon 35/50/15 by Weight	NOMEX®/Protex® 50/50 % by Weight	NOMEX®/Protex® 50/50 % by Weight
Test Description		Value	Value	Value
Basis Weight (oz/y ²)		8	7.8	7.5
Yarn Size (count - warpxfill)		24/2x18/2	24/2x18/2	24/2x18/2
TPP (cal/cm ²)		12.9	13.5	14.9
Vertical Flame Char (inch - warpxfill)		3.8x3.6	3.6x4.1	2.3x2.6
Abrasion (Cycle)		752	651	452
Tear Resistance (lbf - warpxfill)		43x40	41x36	42x39
Grab Strength (lbf - warpxfill)		170x161	177x150	181x164